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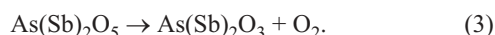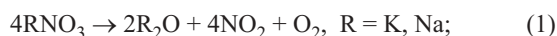
THE EFFECT OF BASICITY OF GLASS ON INTERACTION OF VARIABLE-VALENCE ELEMENTS

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The interaction between two variable-valence elements (As + Fe and As + Cr) simultaneously present in glasses of the four-component system $K_2O – B_2O_3 – SiO_2 – Al_2O_3$ is investigated. It is demonstrated that as the glass basicity increases, the element to the left of the redox series passes to a higher valence state. Recommendations are issued for correcting concentrations of variable-valence elements for the purpose of optimizing the tint (color shade) in tinted and clear glasses.

Several elements of variable valence are always present in a multicomponent glass. They are introduced via raw materials or specially added into the batch for clarification, decolorizing, or tinting glass melt. It is known [1] that clarification in glasses with additives of arsenic or antimony oxides proceeds according to the reactions

$$4RNO_3 \rightarrow 2R_2O + 4NO_2 + O_2, \;\; R = K, Na; \quad (1)$$

$$As(Sb)_2O_3 + O_2 \rightarrow As(Sb)_2O_5; \quad (2)$$

$$As(Sb)_2O_5 \rightarrow As(Sb)_2O_3 + O_2. \quad (3)$$

Saltpeter, which is an obligatory batch component for glass clarification using the above oxides, decomposes in heating according to reaction (1), releasing oxygen. In batch charging, reaction (2) takes place. Increasing temperature in the course of clarification initiates the reverse process (3). The released oxygen penetrates into the bubbles, whose size grows, and the bubbles float, which leads to clarification of the glass melt.

To eliminate the yellow shade caused by the presence of iron(II) oxide, chemical decolorizing agents are introduced into batches of household and technical glasses. As a consequence, iron(III) oxide is formed, which, in contrast to iron(II) oxide, does not have absorption spectra in the visible spectrum range:

$$As(Sb)_2O_5 + FeO \rightarrow As(Sb)_2O_3 + Fe_2O_3. \quad (4)$$
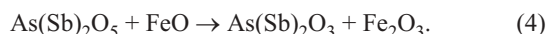
To tint various-purpose glasses, *d*- and *f*-elements, such as iron, copper, chromium, manganese, etc., are widely used. They coexist in glass in several valent forms, each having a higher or a lower tinting capacity. The redox equilibrium between the valent forms depends on many factors: time-temperature melting conditions, oxygen concentration in the furnace atmosphere, content of the variable-valence oxide, glass composition, etc. Since frequently several *d*-elements are simultaneously present in glass, it is important to know the regularities responsible for the equilibrium of variable-valence elements when they are present simultaneously.

Glasses of the four-component system $K_2O – B_2O_3 – SiO_2 – Al_2O_3$ were selected for investigation. The clarifying agent was arsenic oxide, and the second variable-valence element was chromium (series A) or iron (series B). The batches were prepared from the raw materials listed in Table 1.

Table 2 contains the compositions of glasses investigated and the combinations of variable-valence elements considered.

Glass was melted in platinum crucibles at temperatures of 1380 – 1480°C; the melt was stirred with a platinum agitator. Annealed samples were used to produce plane-parallel polished plates of different thickness. The spectral absorp-

TABLE 1

Oxide, element	Chemical compound	Grade of material
SiO_2	SiO_2	Ultra-pure 12-4 (TU 6-09-3379–79)
Al_2O_3	Al_2O_3	Chemically pure for light engineering (TU 6-09-20-11–74)
B_2O_3	H_3BO_3	Ultra-pure 12-3 (TU 6-09-597–77)
K_2O	KNO_3	Ultra-pure 7-4 (TU 6-09-354–75)
K_2O	K_2CO_3	Ultra-pure 11-2 (TU 6-09-2831–78)
As_2O_3	As_2O_3	Refined grade
Cr	$K_2Cr_2O_7$	Pure for analysis (GOST 4220–75)
Fe	Fe_2O_3	Ultra-pure 2-4 (GOST 6-09-1418–78)

TABLE 2

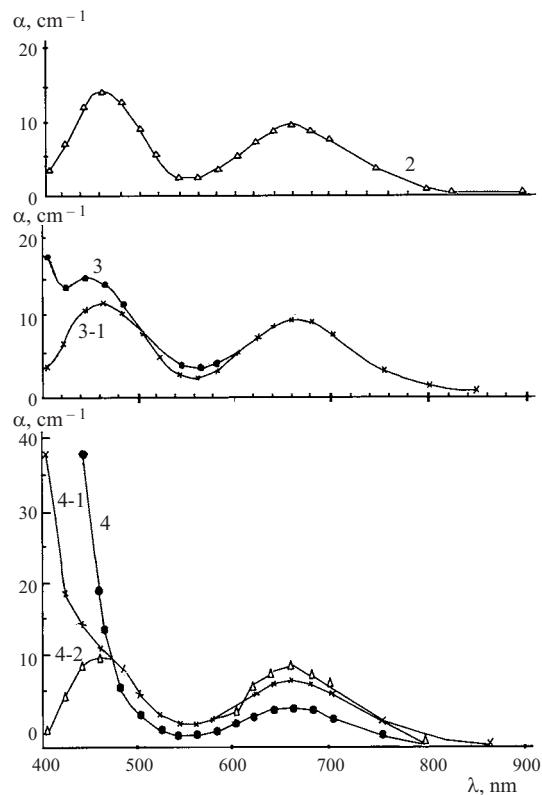| Glass	Molar content,[*] %			Mass content of variable-valence elements, %		
	SiO_2	B_2O_3	K_2O	As_2O_3	Cr	Fe
	Series A					
1	73.5	15.0	9.5	0.2	0.05	–
2	69.0	15.0	14.0	0.2	0.05	–
3	66.0	15.0	17.0	0.2	0.05	–
3-1	66.0	15.0	17.0	1.0	0.05	–
4	60.0	15.0	23.0	0.2	0.05	–
4-1	60.0	15.0	23.0	1.0	0.05	–
4-2	60.0	15.0	23.0	1.0	0.025	–
	Series B					
5	73.5	15.0	9.5	0.2	–	0.3
6	69.0	15.0	14.0	0.2	–	0.3
7	66.0	15.0	17.0	0.2	–	0.3
8	60.0	15.0	23.0	0.2	–	0.3
9	62.2	18.8	17.0	0.2	–	0.3
10	70.3	10.7	17.0	0.2	–	0.3

[*] Al_2O_3 molar content in all cases amounted to 2%.

Fig. 1. Absorption spectral curves of chromium-tinted glasses of series A. Curve numbers correspond to glass numbers in Table 3.

tion indexes of glasses were measured on a SF-16 spectrophotometer in a wavelength range of 400 – 1100 nm.

Glasses containing chromium (series A). Chromium in glass is present in two valence states: Cr(VI) and Cr(III). The spectral absorption curve of trivalent chromium has two absorption bands around 450 and 650 nm, their position may slightly vary depending on the glass composition. The spectrum of hexavalent chromium has an absorption maximum in the ultraviolet range and absorption of Cr(VI) approaches zero when the wavelength is over 600 nm. The colorant capacity of trivalent chromium in the visible range is significantly higher than that of hexavalent chromium [2]. According to data in [1], variable-valence elements present in glasses interact according to the following redox sequence:

$$CrO_3 \leftrightarrow Mn_2O_3 \leftrightarrow CeO_2 \leftrightarrow CuO \leftrightarrow$$
$$As_2O_5 \leftrightarrow Sb_2O_5 \leftrightarrow Fe_2O_3;$$

$$Cr_2O_3 \leftrightarrow MnO \leftrightarrow Ce_2O_3 \leftrightarrow Cu_2O \leftrightarrow$$
$$As_2O_3 \leftrightarrow Sb_2O_3 \leftrightarrow FeO.$$
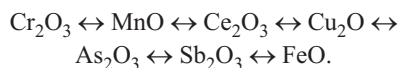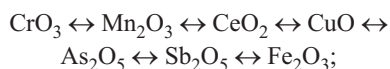
Each left-standing oxide of the upper series that has higher valence is capable of oxidizing any right-positioned oxide of the lower series existing in a lower valence state. Accordingly, it can be expected that the following reaction will take place between arsenic oxide and chromium:

$$3As_2O_3 + 2K_2Cr_2O_7 \rightarrow 3As_2O_5 + 2Cr_2O_3 + 2K_2O. \quad (5)$$

A calculation based on reaction (5) indicated that 0.1427 wt.% As_2O_3 is required to convert 0.05 wt.% hexavalent chromium (the maximum chromium content in series A) to the trivalent state. In practice, 0.2% As_2O_3 was introduced into compositions 1 – 4, and 1.0% As_2O_3 was introduced into compositions 3-1, 4-1, and 4-2. Theoretically, that should be

quite sufficient for converting all chromium into the trivalent state. However, analysis of absorption spectra indicates that part of chromium in some of the analyzed glasses remains oxidized.

Figure 1 shows the spectral absorption curves of some glasses in series A. The spectra of glasses 1 (not indicted in Fig. 1) and 2 are typical of trivalent chromium, since they have two maxima at 460 and 660 nm and a minimum at 550 nm. Glass 3, which has a higher K_2O content than the preceding compositions, exhibits enhanced absorption in the violet spectrum range. This shows that 0.2% arsenic oxide has not been sufficient for reduction of chromium. The spectrophotometric method was used to identify the content of colorant impurities in optical glass (OST 2-4728–79) and established that around 20% chromium remains in the hexavalent state. Only a 7-fold increase in As_2O_3 content compared to the theoretically calculated value (1 % in glass 3-1) made it possible to obtain chromium in the trivalent state. Glass 4, which had an even higher content of K_2O than glass 3, required a 14-fold increase in As_2O_3 content to reduce chromium.

The absolute and relative concentrations of chromium and arsenic in different valent forms were calculated, respectively, using the spectrophotometric method and Eq. (5) based on chromium concentrations. Table 3 shows variations in the contents of Cr(III) and As(V) depending on the content of the modifier oxide in the glass and the basicity coefficient.
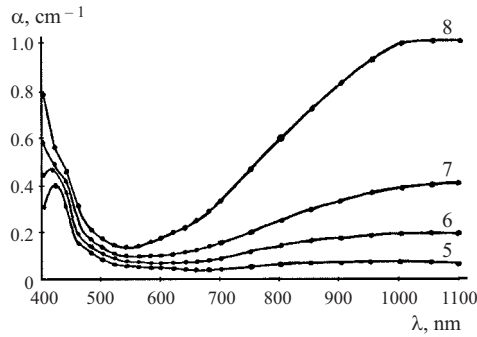
Fig. 2. Absorption spectral curves of iron-tinted glasses of series B. Curve numbers correspond to glass numbers in Table 4.

Thus, the content of K_2O in glass has a strong effect on reactions between the variable-valence elements.

It is known that d-elements in acid glasses tend to decrease their valence, whereas in alkali glasses they tend to increase their valence. The concentration of the alkali metal oxide in the glasses considered varies, and the degree of basicity of glasses was estimated using the basicity coefficient K_{bas} determined according to the expression [3]

$$K_{bas} = \frac{4.6Al_2O_3 + 4.7(K_2O - Al_2O_3)}{0.82SiO_2 + [B_2O_3 - (K_2O - Al_2O_3)]},$$

where SiO_2, B_2O_3, Al_2O_3, and K_2O are the molar contents of oxides, %.

It can be seen from data in Table 3 that for an equal ratio of chromium to arsenic oxide equal to 4, as K_{bas} increases, the content of high-valence Cr(VI) grows from 0 to 65%, and the content of pentavalent arsenic, respectively, drops from 71.4 to 2.5% (glasses 1 – 4), i.e., an increase in glass basicity shifts the equilibria to the right:

$$Cr(III) \rightarrow Cr(VI); \quad As(V) \rightarrow As(III)$$
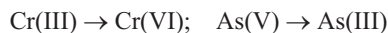
Accordingly, with increasing K_{bas}, the element positioned to the left in the redox series passes to a higher valence state. Therefore, when the reduced form of this element is needed, one should increase the ratio between the concentrations of the less active (i.e., positioned to the right in the redox series) and the more active element. In practice, various-purpose glasses are usually tinted green using chro-

mium (III) oxide, the presence of Cr_2O_3 impairing color being undesirable. Based on the results obtained, when a tinted glass composition changes toward higher basicity, it is recommended to increase the As_2O_3 : Cr ratio in order to prevent an equilibrium shift toward hexagonal chromium.

Iron-containing glasses (series B). Figure 2 shows spectral absorption curves of iron-tinted glasses. As the content of silica decreases (i.e., the basicity of glass increases), the absorption band edge shifts toward longer waves, and absorption intensity in the IR-range caused by the presence of Fe(II) increases. The content of $d_{Fe(II)}$ is indicated in Table 4. It was calculated based on the expression [4]

$$d_{Fe(II)} = \frac{\alpha_{\lambda, Fe}}{\pi_{\lambda, Fe(II)}\rho},$$

where $\alpha_{\lambda, Fe}$ is the specific absorption index of iron for wavelength 900 or 1000 nm, cm^{-1} per 1 wt.% of iron; $\pi_{\lambda, Fe(II)}$ is the volume absorption index of bivalent iron calculated for a concentration equal to 1 g per 100 cm^3 of glass (it is equal to 2.26 cm^2/g for $\lambda = 900$ nm and 3.6 cm^2/g for $\lambda = 1000$ nm); ρ is the glass density, g/cm^3.

The specific absorption index of iron was calculated from the expression

$$\alpha_{\lambda, Fe} = \frac{-\log\tau_\lambda - D_{\rho\lambda}}{lc},$$

where τ_λ is the light transmission coefficient of the glass sample for wavelength λ; $D_{\rho\lambda}$ is the reflection correction for the same wavelength; l is the glass sample thickness, cm; c is the mass content of iron, %.

The absolute content of As_2O_5 was found based on Eq. (4). The content of As_2O_5 converted from arsenic oxide to arsenic and the content of As(V) are listed in Table 4.

As can be seen, the growth of glass basicity is accompanied by an increase in the content of the low-valence form of iron and the high-valence form As(V), i.e., reaction (4) is shifted to the left. Thus, with increasing glass basicity, the element located to the left in the redox series, in this particular case arsenic, tends to become oxidized.

Arsenic is rather widely used in practical glass melting as a chemical decolorizing agent; therefore, in the case of changes in glass composition (basicity coefficient) or in iron

TABLE 3

Glass	Moral content of K_2O, %	Relative content, %		Glass basicity coefficient
		$Cr(III) : Cr_{tot}$	$As(V) : As_{tot}$	
1	9.5	100.0	71.4	0.656
2	14.0	100.0	71.4	0.943
3	17.0	80.0	11.4	1.473
3-1	17.0	100.0	14.3	1.473
4	23.0	35.0	2.5	2.498
4-1	23.0	51.0	3.5	2.498
4-2	23.0	100.0	7.1	2.498

TABLE 4

Glass	K_{bas}	$d_{Fe(II)}$	Mass content of As(V), %	$As(V) : As_{tot}$, %
5	0.656	0.8	0.0016	1.1
6	0.943	2.2	0.0054	3.6
7	1.473	4.3	0.0087	5.7
8	2.498	10.6	0.0214	14.1
9	1.454	2.4	0.0048	3.2
10	1.493	4.8	0.0097	6.4

content in the initial materials, the concentration of As_2O_3 should be corrected to prevent a shift of the Fe(II) $\leftrightarrow$ Fe(III) equilibrium to the left.

Light transmission of silicate optical crowns. Initial materials introduced into clear optical silicate crowns bring with them impurities of variable-valence iron and chromium, and arsenic or antimony oxides are introduced into batches for clarification. Its is known that Cr(III) in the visible spectrum range absorbs 20 times more than Cr(VI), and bivalent iron colors glasses 5 times more intensely than trivalent iron [2]. It can be assumed that chromium and iron coexisting in acid glasses tend to be present in the form of Cr(III), As(III), and Fe(III), and in alkali glasses in the form of Cr(VI), As(V), and Fe(II). Accordingly, light transmission of acid glasses in the visible spectrum range is expected to be slightly poorer than that of alkali glasses. To validate this assumption, Table 5 compares the degrees of basicity and light transmission categories in 22 clear optical crowns. The data on integral light transmission in the visible spectrum range are taken from GOST 3514–78; from category 00 to category 3, the absorption of glasses consistently increases.

It can be seen that glasses with higher basicity are more transparent in the visible spectrum range, which agrees with the above assumption.

The following conclusions can be drawn from the results obtained.

Variable-valence elements in glasses (iron, chromium, and arsenic) react with each other in accordance with the redox series. In the case of joint presence of two elements, growth in glass basicity leads to oxidation of the element to the left of the redox series. An increase in basicity of glasses containing arsenic oxide facilitates the formation of Cr(VI) and Fe(II).

When improving the composition of chromium-tinted glass toward higher basicity, while wishing to maintain its color characteristics at the same or similar level, the equilib-

TABLE 5

K_{bas}	Number of glass grades, units		
	Total	Light transmission category	
		00-0	1-3
Up to 1	5	1	4
1 – 2	6	4	2
More than 2	11	9	2

rium Cr(III) $\leftrightarrow$ Cr(VI) should be shifted to the left by means of increasing the ratio As_2O_3 : Cr in the batch.

When improving the composition of clear glass toward higher basicity while preserving its color characteristics at the same or similar level without additional contamination of glass with iron, the equilibrium Fe(II) $\leftrightarrow$ Fe(III) should be shifted to the right by decreasing the concentration of arsenic oxide, which is a chemical decolorizer.

For a similar concentration of colorant impurity elements in clear multicomponent glasses clarified by arsenic and/or antimony oxides, compositions with higher basicity have higher light transmission in the visible spectrum range.

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